

UV-crosslinkable hotmelt pressure sensitive adhesives comprising pyrogenic silicas

5 The invention relates to a mixture comprising a radiation-crosslinkable polymer composed of at least 40% by weight of C1 to C 18 alkyl (meth)acrylates (polyacrylate for short), and silica.

10 The invention further relates to the use of the mixture in pressure sensitive adhesives (PSAs), particularly in hotmelt PSAs.

Radiation-crosslinkable polymers and their use as adhesives,
15 e.g., as hotmelt PSAs, are known, for example, from EP-A-246 848 or EP-A-377 199.

In the case of radiation-crosslinkable PSAs the cohesion, i.e., the internal strength of the adhesive film, after the adhesive
20 has been coated onto a backing or support, is achieved by means of subsequent, photochemically induced crosslinking.

Adhesion (sticking to the substrate) and cohesion are divergent performance properties. Measures which bring about an improvement
25 in the adhesion are generally accompanied at the same time by a decrease in the cohesion, and vice versa.

There is therefore a desire for measures which improve both the cohesion and the adhesion, or at least do not improve one of the
30 two properties at the expense of the other. Also of importance is a high level of heat stability of the adhesive bond; that is, the bond should withstand mechanical loads even at relatively high temperatures.

35 Particularly in the case of industrial applications, especially with adhesive assembly tapes, high heat stability is often critical to the use of an adhesive.

Pyrogenic silicas are sold, for example, under the brand name
40 Aerosil® by Degussa. They are used, for example, as fillers or auxiliaries for improving rheology in polymer compositions.

It is an object of the present invention to improve the adhesion, cohesion, and heat stability. We have found that this object is
45 achieved by the mixture described at the outset and by its use as a PSA, particularly a hotmelt PSA.

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The radiation-crosslinkable polymer is composed of at least 40% by weight, preferably at least 60% by weight, with particular preference at least 80% by weight, of C₁-C₁₈ alkyl (meth)acrylates.

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Mention may be made in particular of C₁-C₈ alkyl (meth)acrylates, e.g., methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, and 2-ethylhexyl (meth)acrylate.

- 10 The mixture preferably comprises a photoinitiator, so that the polyacrylate is crosslinkable with UV light. Preferably, the photoinitiator is attached to the polyacrylate.

By irradiation with high-energy light, especially UV light, the photoinitiator brings about crosslinking of the polymer, preferably by means of a chemical grafting reaction of the photoinitiator with a spatially adjacent polymer chain. Crosslinking may take place in particular by insertion of a carbonyl group of the photoinitiator into an adjacent C-H bond to form a -C-C-O-H group.

- The mixture contains preferably from 0.0001 to 1 mol, with particular preference from 0.0002 to 0.1 mol, with very particular preference from 0.0003 to 0.01 mol of the photoinitiator, or of the photoinitiator-active molecule group attached to the polymer, per 100 g of polyacrylate.

- The photoinitiator comprises, for example, acetophenone, benzophenone, benzoin ethers, benzil dialkyl ketals or derivatives thereof.

The photoinitiator is preferably attached to the polyacrylate.

- With particular preference the photoinitiator is one which is incorporated into the polymer chain by means of free-radical copolymerization. For this purpose the photoinitiator preferably contains an acrylic or (meth)acrylic group.

- Suitable copolymerizable photoinitiators are acetophenone derivatives or benzophenone derivatives which contain at least one, preferably one, ethylenically unsaturated group. The ethylenically unsaturated group is preferably an acrylic or methacrylic group.

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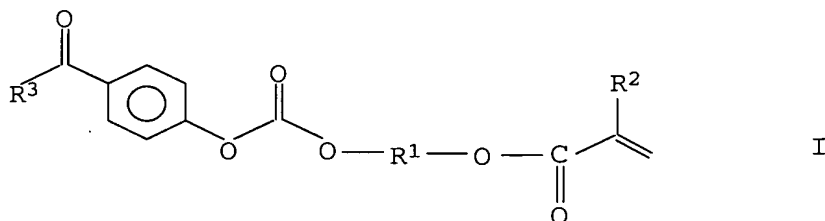
The ethylenically unsaturated group may be attached directly to the phenyl ring of the acetophenone derivative or benzophenone derivative. In general there is a spacer group located between phenyl ring and ethylenically unsaturated group.

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The spacer group may contain, for example, up to 100 carbon atoms.

Suitable acetophenone derivatives or benzophenone derivatives are described, for example, in EP-A-346 734, EP-A-377199 (1st claim), DE-A-4 037 079 (1st claim), and DE-A-3 844 444 (1st claim) and by this reference are hereby incorporated into the present specification. Preferred acetophenone derivatives and benzophenone derivatives are those of the formula

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in which R^1 stands for an organic radical having up to 30 carbon atoms, R^2 for a hydrogen atom or a methyl group, and R^3 for an unsubstituted or substituted phenyl group or a C_1 - C_4 alkyl group.

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R^1 stands with particular preference for an alkylene group, in particular for a C_2 - C_8 alkylene group.

R^3 stands with particular preference for a methyl group or a phenyl group.

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Examples of further monomers of which the polyacrylate may be composed are vinyl esters of carboxylic acids containing up to 20 carbon atoms, vinylaromatics having up to 20 carbon atoms, ethylenically unsaturated nitriles, vinyl halides, vinyl ethers of alcohols containing 1 to 10 carbon atoms, aliphatic hydrocarbons having 2 to 8 carbon atoms and 1 or 2 double bonds, or mixtures of these monomers.

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Suitable vinyl esters include particularly vinyl propionate and with particular preference vinyl acetate.

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Suitable vinylaromatic compounds include, for example, vinyltoluene, α - and p -methylstyrene, α -butylstyrene, 4-n-butylstyrene, 4-n-decylstyrene and, preferably, styrene. Examples of nitriles are acrylonitrile and methacrylonitrile.

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The vinyl halides are ethylenically unsaturated compounds substituted by chlorine, fluorine or bromine, preferably vinyl chloride and vinylidene chloride.

- 5 Examples of vinyl ethers include vinyl methyl ether, vinyl ethyl ether, and vinyl isobutyl ether. Preferred vinyl ethers are those of alcohols containing 1 to 4 carbon atoms.

- As hydrocarbons having 2 to 8 carbon atoms and two olefinic
10 double bonds mention may be made of butadiene, isoprene and chloroprene.

- Further suitable monomers include in particular monomers containing carboxylic acid, sulfonic acid or phosphonic acid
15 groups. Carboxylic acid groups are preferred. Examples that may be mentioned include acrylic acid, methacrylic acid, itaconic acid, maleic acid, and fumaric acid.

- Further monomers are also, for example, hydroxyl-containing
20 monomers, especially C₁-C₁₀ hydroxyalkyl (meth)acrylates, and also (meth)acrylamide.

- Furthermore, mention may be made of phenyloxyethyl glycol mono(meth)acrylate, glycidyl acrylate, glycidyl methacrylate, and
25 amino (meth)acrylates such as 2-aminoethyl (meth)acrylate.

- Monomers which in addition to the double bond carry further functional groups as well, e.g., isocyanate, amino, hydroxy, amide or glycidyl, may, for example, improve the substrate
30 adhesion.

- The polyacrylate preferably has a K value of not more than 80, in particular from 30 to 80, with particular preference from 40 to 60, measured in tetrahydrofuran (1% strength solution, 21°C).
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The Fikentscher K value is a measure of the molecular weight and viscosity of a polymer.

- The glass transition temperature (T_g) in the polyacrylate is
40 preferably from -60 to +10°C, with particular preference from -55 to 0°C, with very particular preference from -55 to -10°C.

- The glass transition temperature of the polyacrylate may be determined by customary methods such as differential
45 thermoanalysis or differential scanning calorimetry (see, for example, ASTM 3418/82, midpoint temperature).

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- The polyacrylates may be prepared by copolymerizing the monomeric components using the customary polymerization initiators and also, where appropriate, regulators, polymerization being carried out at the customary temperatures in bulk, in emulsion, e.g., in water or liquid hydrocarbons, or in solution. Emulsion polymerization produces aqueous dispersions of the polyacrylate. The polyacrylates are preferably prepared by polymerizing the monomers in solvents (solution polymerization), in particular in solvents with a boiling range from 50 to 150°C, preferably from 60 to 120°C, using the customary amounts of polymerization initiators, which are generally from 0.01 to 10% by weight, in particular from 0.1 to 4% by weight, based on the total weight of the monomers. Suitable solvents include, in particular, alcohols, such as methanol, ethanol, n-propanol and isopropanol, n-butanol and isobutanol, preferably isopropanol and/or isobutanol, and also hydrocarbons such as toluene and, in particular, petroleum spirits with a boiling range from 60 to 120°C. It is also possible to use ketones, such as acetone, methyl ethyl ketone, and methyl isobutyl ketone, and esters, such as ethyl acetate, and also mixtures of solvents of the type mentioned, preference being given to mixtures containing isopropanol and/or isobutanol in amounts of from 5 to 95% by weight, in particular from 10 to 80% by weight, preferably from 25 to 60% by weight, based on the solvent mixture used.
- In the case of the solution polymerization, examples of suitable polymerization initiators include azo compounds, ketone peroxides, and alkyl peroxides.
- Following polymerization in solution, the solvents may where appropriate be separated off under reduced pressure, operating at elevated temperatures in the range, for example, from 100 to 150°C. The polymers may then be used in the solvent-free state, i.e., as melts. In some cases it is also of advantage to prepare the polymers by polymerization in bulk, i.e., without the use of a solvent, in which case it is possible to operate batchwise or else continuously, e.g., in accordance with the details of US-PS 4 042 768.
- The polyacrylates used in the mixture of the invention are preferably solvent-free. A residual amount of solvents, e.g., organic solvents and/or water, of below 5 parts by weight, in particular below 2 parts by weight, with particular preference below 1 part by weight, with very particular preference below 0.5 part by weight or below 0.1 part by weight of solvent per 100 parts by weight of polyacrylate, can be present, however.

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The mixture of the invention further comprises silica.

Among synthetic silicas, a distinction is made according to preparation process between precipitated silica and pyrogenic
5 silica.

Pyrogenic silica is preferred. It is obtainable by thermal decomposition of silicone tetrahalides in the presence of oxygen and hydrogen.

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The silica is preferably in powder form. The weight-average diameter of the silica particles is preferably from 5 to 100 nm, with particular preference from 5 to 50 nm.

15 The BET surface area (DIN 66131) is in particular from 20 to 500 m²/g, with particular preference from 50 to 300 m²/g.

The silica is preferably hydrophobically modified. For this purpose it is possible to react free OH groups on the surface
20 with compounds which on the one hand have a group which reacts with OH but otherwise contain hydrophobic groups, especially alkyl groups.

Examples of suitable compounds include silanes, especially
25 chlorosilanes.

The silicas are in particular so hydrophobic that they cannot be dispersed in water (at 21°C).

30 Suitable silicas are available, for example, commercially as Aerosil® (from Degussa).

The silica content of the mixture is preferably from 0.5 to 30 parts by weight, with particular preference from 0.5 to 15 parts
35 by weight, per 100 parts by weight of polyacrylate.

Where the polyacrylate is in the form of an aqueous dispersion, the silica may simply be added to the dispersion.

40 In the preferred case where the polyacrylate has been obtained by solution polymerization in an organic solvent, the silica may simply be added to the solution and then the solvent removed.

This procedure produces particularly advantageous mixtures.

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The mixture is preferably free of water and solvent or contains at most the residual amounts, already indicated above, of less than 5 parts by weight, in particular less than 2 parts by weight; less than 1 part by weight, less than 0.5 part by weight, 5 or less than 0.1 part by weight, of water and/or solvent per 100 parts by weight of polyacrylate.

The mixture of the invention may be used preferably as a pressure sensitive adhesive, and in particular as a hotmelt pressure 10 sensitive adhesive. For this purpose the mixture may consist solely of polyacrylate and silica.

Where photoinitiators have not already been attached to the polyacrylate, they can be added to the mixture at any desired 15 point in time.

Further additives which may be added to the mixture in the case where it is used as a pressure sensitive adhesive (PSA), particularly a hotmelt PSA, are, for example, fillers, dyes, 20 leveling assistants, and, in particular, tackifiers (tackifying resins).

Tackifiers are, for example, natural resins, such as rosins and their derivatives formed by disproportionation or isomerization, 25 polymerization, dimerization and/or hydrogenation. They may be in their salt form (with monovalent or polyvalent counterions, for example (cations)) or, preferably, in their esterified form. Alcohols used for the esterification may be monohydric or polyhydric. Examples are methanol, ethanediol, diethylene glycol, 30 triethylene glycol, 1,2,3-propanetriol, and pentaerythritol.

Use is also made, furthermore, of hydrocarbon resins, e.g., coumarone-indene resins, polyterpene resins, hydrocarbon resins based on unsaturated CH compounds, such as butadiene, pentene, 35 methylbutene, isoprene, piperylene, divinylmethane, pentadiene, cyclopentene, cyclopentadiene, cyclohexadiene, styrene, α -methylstyrene, and vinyltoluene.

Polyacrylates which have a low molar weight are also increasingly 40 being used as tackifiers. These polyacrylates preferably have a weight-average molecular weight M_w of less than 30 000. The polyacrylates are composed preferably of at least 60% by weight, in particular at least 80% by weight, of C_1 - C_8 alkyl (meth)acrylates.

Preferred tackifiers are natural or chemically modified rosins. Rosins are composed predominantly of abietic acid or derivatives of abietic acid.

- 5 The amount by weight of tackifiers is, for example, from 5 to 100 parts by weight, with particular preference from 10 to 50 parts by weight, per 100 parts by weight of polyacrylate (solids/solids).

- 10 The pressure sensitive adhesives are preferably used as hotmelt pressure sensitive adhesives; that is, they are applied to the desired backings or supports from the melt.

- The PSAs and hotmelt adhesives of the invention are particularly
15 suitable for producing self-adhesive articles, such as labels, adhesive tapes or adhesive films, e.g., protective films.

- The self-adhesive articles are generally composed of a backing or support and a film of the adhesive applied to one or both sides,
20 preferably one side.

The backing material may comprise, for example, paper or a polymer film made from polyolefins or PVC.

- 25 The self-adhesive articles are produced in particular by applying the pressure sensitive adhesive to the backing or support and subsequently effecting crosslinking with UV light.

- The self-adhesive articles are suitable for a very wide variety
30 of substrates. The substrates may be made of metals, paper, card, wood, plastics etc.

- It is a particular advantage of the invention that using the pressure sensitive adhesives of the invention very good adhesion
35 is achieved by the self-adhesive articles even on apolar surfaces, particularly on surfaces made of polyolefins, e.g., polyethylene or polypropylene.

- In general, very good adhesion and cohesion are achieved.
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- In particular, there is also an improvement in the heat resistance strength; in other words, the bonds hold even at high temperatures. The mixtures and pressure sensitive adhesives of the invention are particularly suitable as well for adhesive
45 assembly tapes which are employed in the industrial production, for example, of motor vehicles.

Examples

1. Starting materials

5 The polymer was composed of

94.7% by weight n-butyl acrylate

5% by weight acrylic acid

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0.3% by weight photoinitiator of the formula I.

The polymerization was conducted at 100°C in isobutanol solvent at a solids content of 85%. The K value of the polymer was 50. The

15 silica was added at the end of the polymerization as indicated in table 1. Thereafter, the solvent was removed by distillation.

The silica used was Aerosil® from Degussa.

20		BET surface area (m ² /g)	Average particle size (nm)
	Aerosil R812S	220 ± 25	7
	Aerosil R972	110 ± 20	16

25 The resultant hotmelt PSAs had the following composition:

30		Filler	Parts by weight per 100 parts by weight of the above polymer
	H1	0	0
	H2	Aerosil® R812S	3
	H3	Aerosil® R972	3
	H4	Aerosil® R812S	6

35 Performance testing

Hotmelt PSAs H1 - H4 were coated with an application rate of 80 g/m² onto polyester film (Hostaphan RN 36), placed on a conveyor belt and irradiated with 30 mJ/cm² (UV-C² radiation).

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This was followed by measurements of the peel strength (adhesion) and shear strength (cohesion) and of the heat resistance.

45 The PSA-coated backing or support was cut into test strips 25 mm wide. To determine the shear strength the test strips were bonded with an area of 25 mm² to a chromed V2A stainless steel test plate, rolled on once with a 1 kg roller, stored for 10 minutes

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(under standard conditions, 50% relative humidity, 1 bar, 23°C) and then loaded in suspended form with a 1 kg weight (under standard conditions). The measure of the shear strength was the time until the weight fell off; in each case the average from 5 measurements was calculated.

For the measurement of the peel strength (adhesion) a 2.5 cm wide test strip was bonded to a chromed V2A stainless steel test plate and rolled on once with a 1 kg roller. It was then clamped by one end into the upper jaw of a stress/strain testing apparatus. The adhesive strip was pulled from the test area at 300 mm/min at an angle of 180°, i.e., the test strip was bent over and pulled off parallel to the metal test plate, and the force required to do this was measured. The measure of the peel strength was the force, in N/2.5 cm, which was the average of five measurements.

The peel strength was measured 24 hours after bonding. After this time, the bond strength has developed fully.

For the SAFT test (heat resistance) the samples were prepared as for the shear test and loaded with 1 kg. The samples were then suspended in a controlled-drying cabinet and the temperature was raised by 0.5°C/min. The measure used for the heat resistance is the temperature at which the weight falls off.

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Results:

	Shear strength [min]	Peel strength [N/25 mm]	S.A.F.T. Test 1 [°C]	S.A.F.T. Test 2 [°C]	S.A.F.T. Test 3 [°C]
H1	67	22.0	90	109	109
H2	115	26.4	108	> 160	> 160
H3	119	25.3	> 160	> 160	> 160
H4	121	30.4	> 160	> 160	> 160

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We claim:-

1. A mixture comprising a radiation-crosslinkable polymer
5 composed of at least 40% by weight of C1 to C 18 alkyl
(meth)acrylates (polyacrylate for short), and silica.
2. A mixture as claimed in claim 1, wherein the polyacrylate is
prepared by solution polymerization in an organic solvent.
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3. A mixture as claimed in claim 1 or 2, wherein the
polyacrylate has a Fikentscher K value of from 30 to 80 (in
1% strength solution in tetrahydrofuran solvent at 21°C).
- 15 4. A mixture as claimed in any of claims 1 to 3, wherein the
polyacrylate is crosslinkable by UV light.
5. A mixture as claimed in any of claims 1 to 4, comprising a
photoinitiator.
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6. A mixture as claimed in claim 5, wherein the photoinitiator
is attached to the polyacrylate.
7. A mixture as claimed in any of claims 1 to 6, wherein the
25 silica comprises pyrogenic silica.
8. A mixture as claimed in any of claims 1 to 7, wherein the
silica has a weight-average particle diameter of from 5 to
100 nm.
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9. A mixture as claimed in any of claims 1 to 8, wherein the
silica is hydrophobically modified.
10. A mixture as claimed in any of claims 1 to 9, wherein the
35 silica content is from 0.5 to 30 parts by weight per 100
parts by weight of polyacrylate.
11. A mixture as claimed in any of claims 1 to 10, obtainable by
adding the silica to the organic solution of the polyacrylate
40 and then separating off the solvent.

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12. A mixture as claimed in any of claims 1 to 11, wherein the amount of water and organic solvents is less than 5 parts by weight per 100 parts by weight of polyacrylate.

5 13. A pressure sensitive adhesive comprising a mixture as claimed in any of claims 1 to 12.

14. A hotmelt pressure sensitive adhesive comprising a mixture as claimed in any of claims 1 to 12.

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15. A process for producing self-adhesive articles, which comprises applying a pressure sensitive adhesive or hotmelt pressure sensitive adhesive as claimed in claim 13 or 14 to substrates, e.g., labels, adhesive tapes or films, and

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subsequently effecting crosslinking by UV light.

16. The use of the adhesive of claim 13 or 14 for producing self-adhesive articles.

20 17. The use of the adhesive of claim 13 or 14 for producing adhesive assembly tapes.

18. A self-adhesive article, particularly an adhesive assembly tape, obtainable by a process as claimed in claim 15 or by

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using an adhesive as claimed in claim 13 or 14.

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UV-crosslinkable hotmelt pressure sensitive adhesives comprising pyrogenic silicas

5 Abstract

A mixture comprising a radiation-crosslinkable polymer composed of at least 40% by weight of C1 to C18 alkyl (meth)acrylates (polyacrylate for short), and silica.

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